

THAT WHICH IS CLAIMED:

1. A positive electrode active material for secondary lithium and lithium-ion batteries comprising:

5 at least one electron conducting compound having the formula $\text{LiM}^1_{x-y}\{\text{A}\}_y\text{O}_z$ wherein M^1 is a transition metal; $\{\text{A}\}$ is represented by the formula $\sum w_i \text{B}_i$ wherein B_i is an element other than M^1 used to replace the transition metal M^1 and w_i is the fractional amount of element B_i in the total dopant combination such that $\sum w_i = 1$; B_i is a cation in $\text{LiM}^1_{x-y}\{\text{A}\}_y\text{O}_z$; $0.95 \leq x \leq 1.05$; $0 \leq y \leq x/2$; and $1.90 \leq z \leq 2.10$; and

10 at least one electron insulating and lithium ion conducting lithium metal oxide.

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2. The positive electrode active material according to Claim 1, wherein the lithium metal oxide is selected from the group consisting of LiAlO_2 and $\text{Li}_2\text{M}^2\text{O}_3$, wherein M^2 is at least one tetravalent metal selected from the group consisting of Ti, Zr, Sn, Mn, Mo, Si, Ge, Hf, Ru and Te.

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3. The positive electrode active material according to Claim 2, wherein the lithium metal oxide is selected from the group consisting of Li_2TiO_3 , Li_2ZrO_3 and mixtures thereof.

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4. The positive electrode active material according to Claim 2, wherein the lithium metal oxide is Li_2TiO_3 .

25 5. The positive electrode active material according to Claim 1, comprising from greater than or equal to 95% by weight and less than 100% by weight of $\text{LiM}^1_{x-y}\{\text{A}\}_y\text{O}_z$ and greater than 0% by weight and less than or equal to 5% by weight of the lithium metal oxide.

6. The positive electrode active material according to Claim 1, wherein M^1 is selected from the group consisting of Co, Ni, Mn and Ti.

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7. The positive electrode active material according to Claim 1, wherein $x=1$ and $z=2$.

8. The positive electrode active material according to Claim 7, wherein M^1 is
5 Ni.

9. The positive electrode active material according to Claim 7, wherein M^1 is
Co.

10 10. The positive electrode active material according to Claim 1, wherein $y > 0$.

11. The positive electrode active material according to Claim 10, wherein the
dopant elements B_i are selected from the group consisting of elements having a Pauling's
electronegativity not greater than 2.05, Mo, Te and Ru.

15 12. The positive electrode active material according to Claim 10, wherein the
dopant elements B_i include two or more dopant cations.

13. The positive electrode active material according to Claim 12, wherein the
20 average oxidation state E of the dopant elements B_i , as determined using the formula
 $E = \sum w_i E_i$ wherein E_i is the oxidation state of dopant element B_i in the lithium metal
oxide $LiM^{1-x-y}\{A\}_yO_z$, is represented by the relationship $2.5 \leq E \leq 3.5$.

14. The positive electrode active material according to Claim 13, wherein
25 $2.9 \leq E \leq 3.1$.

15. The positive electrode active material according to Claim 13, wherein
 $E=3$.

16. The positive electrode active material according to Claim 12, wherein at least one of the dopant elements B_i has a different oxidation state than M^1 in $LiM^{1-x-y}\{A\}_yO_z$.

5 17. The positive electrode active material according to Claim 12, wherein at least two of the dopant elements B_i have a different oxidation state than M^1 in $LiM^{1-x-y}\{A\}_yO_z$.

10 18. The positive electrode active material according to Claim 1, wherein x, y and z are values that provide a stable lithium metal oxide compound.

15 19. The positive electrode active material according to Claim 2, wherein the metal M^2 is present in $LiM^{1-x-y}\{A\}_yO_z$ as M^1 or as a dopant element B_i or Al is present as a dopant element B_i .

20. The positive electrode active material according to Claim 19, wherein the lithium metal oxide has the formula $Li_2M^2O_3$ and M^2 includes Ti.

20 21. The positive electrode active material according to Claim 2, wherein M^1 is Ni or Co, M^2 is Ti, and the dopant elements B_i include Ti^{4+} and Mg^{2+} .

22. The positive electrode active material according to Claim 21, wherein M^1 is Ni.

25 23. The positive electrode active material according to Claim 22, wherein the dopant elements B_i further include Co^{3+} .

24. The positive electrode active material according to Claim 22, wherein the dopant elements B_i further include Li^+ cations.

25. The positive electrode active material according to Claim 1, wherein the
LiM¹_{x-y}{A}_yO₂ compound has the formula LiNi_{1-y}Co_aM³_bM⁴_cO₂, wherein M³ is selected
from the group consisting of Ti, Zr, and combinations thereof; M⁴ is selected from the
group consisting of Mg, Ca, Sr, Ba, and combinations thereof; y=a+b+c, 0 < y ≤ 0.5;
5 0 < a < 0.5; 0 < b ≤ 0.15; and 0 < c ≤ 0.15.

26. The positive electrode active material according to Claim 25, wherein
0.1 ≤ a ≤ 0.3.

10 27. The positive electrode active material according to Claim 25, wherein M³
includes Ti.

15 28. The positive electrode active material according to Claim 27, wherein M⁴
includes Mg.

29. The positive electrode active material according to Claim 25, further
comprising at least one metal oxide of the formula M³O₂.

30. The positive electrode active material according to Claim 29, wherein M³
20 includes Ti and said metal oxide is TiO₂.

31. The positive electrode active material according to Claim 1, further
comprising at least one electron insulating and lithium-ion conducting metal oxide.

25 32. The positive electrode active material according to Claim 31, wherein the
metal oxide has the formula MO₂ wherein M is at least one tetravalent metal selected
from the group consisting of Ti, Zr, Sn, Mo, Si, Ge, Hf, Ru and Te.

30 33. The positive electrode active material according to Claim 32, wherein
M=M².

34. The positive electrode active material according to Claim 33, wherein said metal oxide is TiO_2 .

5 35. A positive electrode for a secondary lithium or lithium-ion battery comprising the positive electrode active material of Claim 1, a carbonaceous material and a polymer binder.

10 36. A secondary lithium or lithium-ion battery comprising a positive electrode, a negative electrode and a nonaqueous electrolyte, wherein the positive electrode includes the positive electrode active material of Claim 1.

15 37. A positive electrode active material for secondary lithium and lithium-ion batteries comprising at least one compound of the formula $LiM^{1-x-y}\{A\}_yO_z$ and at least one lithium metal oxide selected from the group consisting of $LiAlO_2$ and $Li_2M^2O_3$, wherein M^1 is a transition metal, M^2 is at least one tetravalent metal selected from the group consisting of Ti, Zr, Sn, Mn, Mo, Si, Ge, Hf, Ru and Te, $\{A\}$ is represented by the formula $\sum w_i B_i$ wherein B_i is an element other than M^1 used to replace the transition metal M^1 and w_i is the fractional amount of element B_i in the total dopant combination such that $20 \sum w_i = 1$; B_i is a cation in $LiM^{1-x-y}\{A\}_yO_z$; $0.95 \leq x \leq 2.10$; $0 \leq y \leq x/2$; and $1.90 \leq z \leq 4.20$.

25 38. The positive electrode active material according to Claim 37, wherein the lithium metal oxide is selected from the group consisting of Li_2TiO_3 , Li_2ZrO_3 and mixtures thereof.

39. The positive electrode active material according to Claim 38, wherein the lithium metal oxide is Li_2TiO_3 .

40. The positive electrode active material according to Claim 37, comprising from greater than or equal to 95% by weight and less than 100% by weight of $\text{LiM}^1_{x-y}\{\text{A}\}_y\text{O}_z$ and greater than 0% by weight and less than or equal to 5% by weight of the lithium metal oxide.

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41. The positive electrode active material according to Claim 37, wherein $x=1$ and $z=2$.

42. The positive electrode active material according to Claim 37, wherein $x=2$
10 and $z=4$.

43. The positive electrode active material according to Claim 37, wherein M^1 is selected from Co, Ni, Mn, Ti, Fe, Cr, V and Mo.

15 44. The positive electrode active material according to Claim 37, wherein M^1 is selected from Co, Ni, Mn and Ti.

45. The positive electrode active material according to Claim 37, wherein
20 $y > 0$.

46. The positive electrode active material according to Claim 45, wherein the dopant elements B_i are selected from the group consisting of elements having a Pauling's electronegativity not greater than 2.05, Mo, Te and Ru.

25 47. The positive electrode active material according to Claim 45, wherein the dopant elements B_i includes two or more dopant cations.

48. The positive electrode active material according to Claim 47, wherein the average oxidation state E of the dopant elements B_i , as determined using the formula
30 $E = \sum w_i E_i$ wherein E_i is the oxidation state of dopant element B_i in the lithium metal

oxide $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$, equals the oxidation state of the replaced transition metal ion $M^1 \pm 0.5$.

49. The positive electrode active material according to Claim 48, wherein E
5 equals the oxidation state of the replaced transition metal ion $M^1 \pm 0.1$.

50. The positive electrode active material according to Claim 48, wherein E
equals the oxidation state of the replaced transition metal ion M^1 .

10 51. The positive electrode active material according to Claim 47, wherein at
least one of the dopant elements B_i has a different oxidation state than M^1 in
 $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$.

15 52. The positive electrode active material according to Claim 47, wherein at
least two of the dopant elements B_i have a different oxidation state than M^1 in
 $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$.

53. The positive electrode active material according to Claim 37, wherein x, y
and z are values that provide a stable lithium metal oxide compound.

20 54. The positive electrode active material according to Claim 37, wherein the
metal M^2 is present in $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$ as M^1 or as a dopant element B_i , or Al is present as
a dopant element B_i .

25 55. The positive electrode active material according to Claim 54, wherein the
lithium metal oxide has the formula $\text{Li}_2\text{M}^2\text{O}_3$ and M^2 includes Ti.

56. The positive electrode active material according to Claim 37, further
comprising at least one electron insulating and lithium ion conducting metal oxide.

57. The positive electrode active material according to Claim 56, wherein the metal oxide has the formula MO_2 wherein M is at least one tetravalent metal selected from the group consisting of Ti, Zr, Sn, Mo, Si, Ge, Hf, Ru and Te.

5 58. The positive electrode active material according to Claim 57, wherein $M=M^2$.

10 59. The positive electrode active material according to Claim 57, wherein said metal oxide is TiO_2 .

60. A positive electrode for a secondary lithium or lithium-ion battery comprising the positive electrode active material of Claim 37, a carbonaceous material and a binder polymer.

15 61. A secondary lithium or lithium-ion battery comprising a positive electrode, a negative electrode and a nonaqueous electrolyte, wherein the positive electrode includes the positive electrode active material of Claim 37.

20 62. A method of preparing a positive electrode active material for secondary lithium and lithium-ion batteries, the positive electrode active material including separate lithium metal oxide phases corresponding to the formulas $LiM^{1-x-y}\{A\}_yO_z$ and $Li_2M^2O_3$ or $LiAlO_2$, comprising the steps of:

25 intimately mixing source compounds containing M^1 , Li and optionally {A} in amounts sufficient to provide a stoichiometric relationship between M^1 , Li and {A} corresponding to the formula $LiM^{1-x-y}\{A\}_yO_z$ wherein M^1 is a transition metal, {A} is represented by the formula $\sum w_i B_i$ wherein B_i is an element other than M^1 used to replace the transition metal M^1 and w_i is the fractional amount of element B_i in the total dopant combination such that $\sum w_i = 1$; B_i is a cation in $LiM^{1-x-y}\{A\}_yO_z$; at least one of M^1 and B_i is selected from the group consisting of Ti, Zr, Sn, Mn, Mo, Si, Al, Ge, Hf, Ru and Te;

30 $0.95 \leq x \leq 2.10$; $0 \leq y \leq x/2$; and $1.90 \leq z \leq 4.20$;

firing the mixture in the presence of oxygen at an initial firing temperature and optionally one or more additional firing temperatures, at least one of said initial firing temperature and optionally one or more additional firing temperatures being the maximum firing temperature and at least one of said initial firing temperature and

5 optionally one or more additional firing temperatures being between about 700°C and about 1000°C, wherein said firing step comprises heating the mixture at a sufficiently slow rate from 500°C to the maximum firing temperature to produce separate lithium metal oxide phases including $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$ and LiAlO_2 or $\text{Li}_2\text{M}^2\text{O}_3$, wherein M^2 is one of M^1 and B_i , and M^2 is selected from the group consisting of Ti, Zr, Sn, Mn, Mo, Si, Ge,

10 Hf, Ru and Te; and

cooling the $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$ and $\text{Li}_2\text{M}^2\text{O}_3$ or LiAlO_2 compounds.

63. The method according to Claim 62, wherein said firing step comprises heating the mixture from 500°C to the maximum firing temperature at an average rate of

15 less than or equal to about 10°C/min.

64. The method according to Claim 62, wherein said firing step comprises heating the mixture at a sufficiently slow rate from 500°C to the maximum firing temperature to produce separate lithium metal oxide phases including $\text{LiM}^1_{x-y}\{A\}_y\text{O}_z$,

20 $\text{Li}_2\text{M}^2\text{O}_3$ and M^2O_2 , wherein one of M^1 and B_i is M^2 and M^2 is selected from the group consisting of Ti, Zr, Sn, Mo, Si, Ge, Hf, Ru and Te.

65. The method according to Claim 64, wherein said mixing step comprises mixing source compounds wherein one of M^1 and B_i is selected from the group

25 consisting of Ti and Zr.

66. The method according to Claim 65, wherein said mixing step comprises mixing source compounds wherein one of M^1 and B_i is Ti.

67. The method according to Claim 62, wherein said mixing step comprises dry mixing the source compounds.

68. The method according to Claim 62, wherein said mixing step comprises 5 preparing a solution comprising M^1 and {A} from source compounds comprising M^1 and {A}, precipitating the M^1 and {A} out of solution to produce an intimately mixed hydroxide and blending the mixed hydroxide with a lithium source compound.

69. The method according to Claim 62, wherein said firing step comprises 10 firing the mixture at a partial pressure of oxygen of at least 20 kPa.

70. The method according to Claim 62, wherein one of M^1 and B_i is selected from the group consisting of Ti, Zr, Sn, Mn, Mo, Si, Ge, Hf, Ru and Te.

71. The method according to Claim 62, wherein said mixing step comprises 15 mixing source compounds such that one of M^1 and B_i is Ti.

72. The method according to Claim 62, wherein said firing step comprises heating the mixture at a sufficiently slow rate from 500°C to the maximum firing 20 temperature to produce separate lithium metal oxide phases including $LiM^{1-x-y}\{A\}_yO_z$ and $Li_2M^2O_3$ or $LiAlO_2$ such that the lithium metal oxide phases include greater than or equal to 95% by weight and less than 100% by weight of $LiM^{1-x-y}\{A\}_yO_z$ and greater than 0% by weight and less than or equal to 5% by weight of $Li_2M^2O_3$.

73. The method according to Claim 62, wherein said mixing step comprises 25 mixing source compounds containing a transition metal M^1 selected from the group consisting of Co, Ni, Mn, Ti, Fe, Cr, V and Mo.

74. The method according to Claim 62, wherein said mixing step comprises mixing source compounds containing a transition metal M^1 is selected from Co, Ni, Mn and Ti.

5 75. The method according to Claim 62, wherein said mixing step comprises mixing source compounds including dopant elements B_i such that $y > 0$.

10 76. The method according to Claim 75, wherein said mixing step comprises mixing source compounds including dopant elements B_i selected from the group consisting of elements having a Pauling's electronegativity not greater than 2.05, Mo, Te and Ru.

15 77. The method according to Claim 75, wherein said mixing step comprises mixing source compounds including two or more dopant elements B_i .

78. The method according to Claim 77, wherein said mixing step comprises mixing source compounds wherein the average oxidation state E of the dopant elements B_i , as determined using the formula $E = \sum w_i E_i$ wherein E_i is the oxidation state of dopant element B_i in the lithium metal oxide $LiM^{1-x-y}\{A\}_yO_z$, equals the oxidation state of the 20 replaced transition metal ion $M^{1 \pm 0.5}$.

25 79. The method according to Claim 77, wherein said mixing step comprises mixing source compounds wherein the average oxidation state E of the dopant elements B_i , as determined using the formula $E = \sum w_i E_i$ wherein E_i is the oxidation state of dopant element B_i in the lithium metal oxide $LiM^{1-x-y}\{A\}_yO_z$, equals the oxidation state of the 30 replaced transition metal ion $M^{1 \pm 0.1}$.

80. The method according to Claim 77, wherein said mixing step comprises mixing source compounds wherein the average oxidation state E of the dopant elements B_i , as determined using the formula $E = \sum w_i E_i$ wherein E_i is the oxidation state of dopant

element B_i in the lithium metal oxide $LiM^{1-x-y}\{A\}_yO_z$, equals the oxidation state of the replaced transition metal ion M^1 .

81. The method according to Claim 77, wherein said mixing step comprises
5 mixing source compounds wherein at least one of the dopant elements B_i has a different
oxidation state than M^1 in $LiM^{1-x-y}\{A\}_yO_z$.

82. The method according to Claim 77, wherein said mixing step comprises
mixing source compounds wherein at least two of the dopant elements B_i has a different
10 oxidation state than M^1 in $LiM^{1-x-y}\{A\}_yO_z$.

83. The method according to Claim 77, wherein said mixing step comprises
mixing source compounds in amounts sufficient to provide values for x, y and z that
provide a stable metal oxide compound.

15 84. The method according to Claim 62, wherein said mixing step comprises
mixing the source compounds in amounts sufficient to produce a $LiM^{1-x-y}\{A\}_yO_z$
compound wherein $x=1$ and $z=2$.

20 85. The method according to Claim 84, wherein said mixing step comprises
mixing source compounds containing Ni or Co as the transition metal M^1 .

86. The method according to Claim 85, wherein said mixing step comprises
mixing source compounds containing Ti^{4+} and Mg^{2+} as dopant elements B_i .

25 87. The method according to Claim 86, wherein said mixing step comprises
mixing source compounds containing Ni as the transition metal M^1 .

88. The method according to Claim 87, wherein said mixing step comprises
30 mixing source compounds further including Co^{3+} as a dopant element B_i .

89. The method according to Claim 85, wherein said mixing step comprises mixing source compounds further including Li^+ as a dopant element B_i .

5 90. The method according to Claim 85, wherein said mixing step comprises mixing source compounds containing Co as the transition metal M^1

91. The method according to Claim 62, wherein said mixing step comprises mixing source compounds containing Li, Ni, Co, M^3 and M^4 in amounts sufficient to
10 provide a stoichiometric relationship between Li, Ni, Co, M^3 and M^4 corresponding to the formula $\text{LiNi}_{1-y}\text{Co}_a\text{M}^3{}_{b}\text{M}^4{}_{c}\text{O}_2$ wherein M^3 is selected from the group consisting of Ti, Zr, and combinations thereof; M^4 is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof; M^2 is M^3 ; $y=a+b+c$, $0 < y \leq 0.5$; $0 < a < 0.5$; $0 < b \leq 0.15$; and $0 < c \leq 0.15$.

15 92. The method according to Claim 62, wherein said mixing step comprises mixing the source compounds in amounts sufficient to produce a $\text{LiM}^1{}_{x-y}\{\text{A}\}_y\text{O}_z$ compound wherein $x=2$ and $z=4$.

20 93. The method according to Claim 62, wherein said cooling step comprises cooling the $\text{LiM}^1{}_{x-y}\{\text{A}\}_y\text{O}_z$ and $\text{Li}_2\text{M}^2\text{O}_3$ or LiAlO_2 compounds at a rate of greater than or equal to about $0.5^\circ\text{C}/\text{min}$ and less than or equal to about $140^\circ\text{C}/\text{min}$.

25 94. The method according to Claim 62, wherein said mixing step comprises mixing source compounds such that excess of the source compound containing lithium is provided in the mixture.

95. A method of preparing a positive electrode active material for secondary lithium and lithium-ion batteries, the positive electrode active material including separate

lithium metal oxide phases corresponding to the formulas $\text{LiNi}_{1-y}\text{Co}_a\text{M}^3{}_b\text{M}^4{}_c\text{O}_2$ and $\text{Li}_2\text{M}^3\text{O}_3$ comprising the steps of:

intimately mixing source compounds containing Li, Ni, Co, M^3 and M^4 in amounts sufficient to provide a stoichiometric relationship between Li, Ni, Co, M^3 and M^4 corresponding to the formula $\text{LiNi}_{1-y}\text{Co}_a\text{M}^3{}_b\text{M}^4{}_c\text{O}_2$ wherein M^3 is selected from the group consisting of Ti, Zr and combinations thereof; M^4 is selected from the group consisting of Mg, Ca, Sr, Ba, and combinations thereof; $y=a+b+c$, $0 < y \leq 0.5$; $0 < a < 0.5$; $0 < b \leq 0.15$; and $0 < c \leq 0.15$;

firing the mixture in the presence of oxygen at an initial firing temperature and 10 optionally one or more additional firing temperatures wherein at least one of the firing temperatures is the maximum firing temperature and wherein at least one of the firing temperatures is between about 700°C and about 1000°C, said firing step comprising heating the mixture from 500°C to the maximum firing temperature at an average rate of less than or equal to 10°C/min to produce separate lithium metal oxide phases including 15 $\text{LiNi}_{1-y}\text{Co}_a\text{M}^3{}_b\text{M}^4{}_c\text{O}_2$ and $\text{Li}_2\text{M}^3\text{O}_3$; and cooling the $\text{LiNi}_{1-y}\text{Co}_a\text{M}^3{}_b\text{M}^4{}_c\text{O}_2$ and $\text{Li}_2\text{M}^3\text{O}_3$ compounds.

96. The method according to Claim 95, wherein said mixing step comprises mixing source compounds such that M^3 includes Ti.

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97. The method according to Claim 96, wherein said mixing step comprises mixing source compounds such that M^4 includes Mg.